Role of Tunneling Matrix Elements in Determining the Magnitude of the Tunneling Spin Polarization of 3*d* Transition Metal Ferromagnetic Alloys

Christian Kaiser,[1,2] Sebastiaan van Dijken,[1,*] See-Hun Yang,[1] Hyunsoo Yang,[1] and Stuart S. P. Parkin[1,†]

[1]*IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120, USA*

[2]*2. Physikalisches Institut, RWTH-Aachen, Aachen, Germany*

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We have measured the tunneling spin polarization and associated tunneling magnetoresistance for Co-Pt and Co-V alloys using Al_2O_3 and AlN barriers. These properties are insensitive to the Pt content of Co-Pt alloys for up to 40 at. % Pt, whereas the spin polarization of Co-V alloys decreases significantly with the addition of small amounts of V. We attribute these different behaviors to the relative strengths of bonds formed between the alloy constituents and oxygen in the Al_2O_3 tunnel barrier, which thereby influence the corresponding tunneling rates. The results for AlN barriers are consistent with this argument.

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Recently, magnetic tunnel junctions (MTJs) have generated considerable scientific and technological interest due to their potential application in advanced magnetic recording heads and nonvolatile magnetic random access memories [1–3]. MTJs are composed of two ferromagnetic layers separated by a thin insulating tunnel barrier. The resistance of the tunnel junctions depends on the relative orientation of the magnetic moments of the two electrodes. Switching the magnetic moments from a parallel to an antiparallel alignment can produce large changes in the tunneling resistance exceeding 50% for Al_2O_3 [4,5] and 220% for MgO barriers at room temperature [6]. The tunnel magnetoresistance (TMR) originates from spin-dependent tunneling through the insulating barrier and its magnitude strongly depends on the spin polarization of the ferromagnetic electrodes [7].

The tunneling spin polarization (TSP) of ferromagnetic alloys of Co-Pt and Co-V was measured at 0.25 K using superconducting tunneling spectroscopy (STS) [8] in tunneling junctions with counterelectrodes formed from thin (~45 Å) superconducting aluminum films doped with 2–5 at. % Si [9]. Structures with both Al_2O_3 and AlN barriers were fabricated. Al_2O_3 barriers were formed by plasma oxidizing a 16 Å thick Al layer, whereas AlN barriers, ~35 Å thick, were prepared by reactive rf magnetron sputtering from an Al target in Ar-N_2 (20%). The junctions were prepared by magnetron sputtering through a sequence of metal shadow masks at room temperature on Si substrates covered with ~250 Å SiO_2. The active area of the tunnel junction was $\sim 80 \times 80\ \mu m^2$. Tunneling magnetoresistance studies were carried out on MTJs with ~20 Å thick $Co_{84}Fe_{16}$ electrodes, exchange biased by ~250 Å thick antiferromagnetic $Ir_{25}Mn_{75}$ layers grown on Ta underlayers. Counterelectrodes of ~200 Å thick Co or Fe based alloys capped with Ta layers were used (for more details see Ref. [4]). The magnetization of the ferromagnetic alloys was extracted from SQUID magnetometry measurements on ~1000 Å thick films.

The dependence of the TSP and the magnetization (●) for Co-V and Co-Pt alloys as a function of the atomic fraction of V and Pt, respectively, are compared in Fig. 1. TSP data for Al_2O_3 and AlN barriers are shown as open symbols (□/△) and + signs, respectively. The magnetization of these alloys, measured at 5 K, decreases with increasing amounts of both V and Pt although the rate of decrease is much faster for V than for Pt, as previously found in bulk alloys [10]. Indeed, for V contents exceeding ~35 at. % the alloys become paramagnetic [10]. By contrast, for $Co_{1-x}Pt_x$ alloys, the dependence of the atomic magnetic moment m_{Co-Pt} on Pt content can be approximately fitted by $m_{Co-Pt} = (1 - x)m_{Co}$ which suggests that the Co atoms largely retain their magnetic moment m_{Co} and that the decrease of the total magnetic moment is mostly due to dilution. This simple picture is consistent with x-ray magnetic circular dichroism (XMCD) spectroscopy measurements which we carried out at room temperature on a representative Co-Pt alloy film composed of $Co_{60}Pt_{40}$. These studies show that the Co magnetic moment is only slightly smaller than that of pure Co and that the magnetic moment on Pt is very small. Prior XMCD [11] and neutron scattering [12] measurements on $Co_{50}Pt_{50}$ and $Co_{25}Pt_{75}$ alloys, respectively, also show that the Co moment is similar to bulk Co, even in highly diluted alloys, and that the Pt acquires a small moment of $\sim 0.3\mu_B$ consistent with our data.

We first discuss TSP results for junctions with Al_2O_3 barriers. For $Co_{1-x}V_x$ alloys we find that the TSP decreases rapidly with increasing V fraction x approximately linearly with x. Based on extensive STS measurements on Ni alloyed with a range of various paramagnetic 3*d* transition metals, Meservey and Tedrow concluded that the TSP is proportional to the average atomic magnetic moment of the alloy [13–15]. Consistent with these earlier observations, we do find an approximate linear relationship between TSP and magnetization for these Co-V alloys [see inset of Fig. 1(a)]. However, since the TSP and the mag-

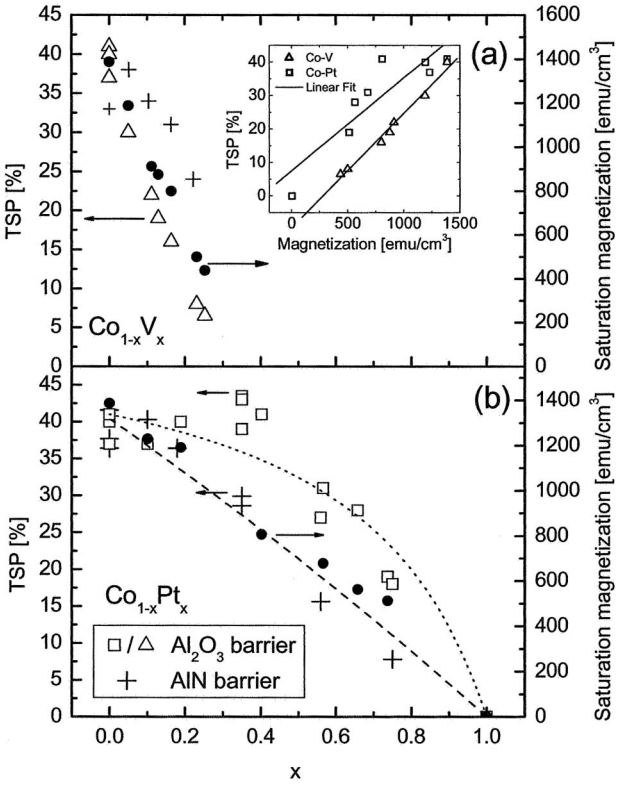

FIG. 1. Tunneling spin polarization at 0.25 K (□, △, and +) and magnetization (●) at 5 K for (a) $Co_{1-x}V_x$ and (b) $Co_{1-x}Pt_x$ alloys as a function of the V and Pt atomic fractions. □/△ and + correspond to samples with Al_2O_3 barriers and AlN barriers, respectively. Note that the TSP values for AlN, which are systematically lower than for Al_2O_3, have been correspondingly scaled for ease of comparison with the results for Al_2O_3 barriers. Scaling factors of 2 and 2.6 were used in (a) and (b), respectively. The lines in (b) are fits to the spin polarization data assuming that the polarization of the electrons tunneling from Co sites is independent of Pt concentration. The fit yields a tunneling probability from Pt sites that is ~3.8 times lower than from Co sites for the case of Al_2O_3 barriers (dotted line) and ~1.1 times lower for the case of AlN barriers (dashed line). The TSP (for Al_2O_3) is plotted versus the corresponding magnetization of the Co-V or Co-Pt alloy in the inset of (a).

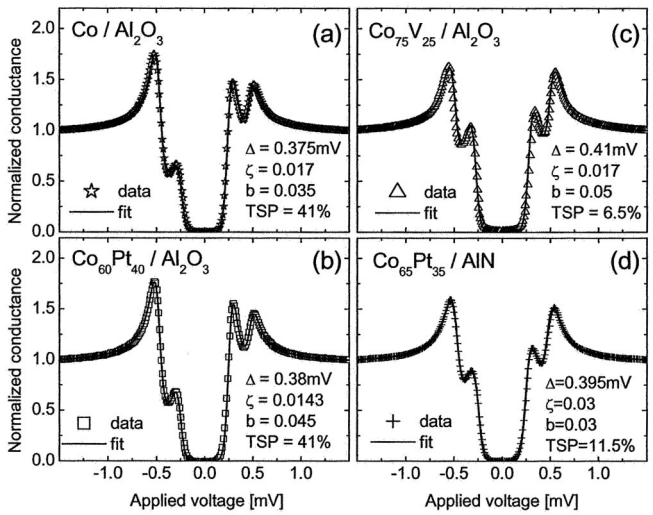

FIG. 2. Conductance versus bias voltage curves (symbols) and fits (lines) for STS junctions with Co, Co-V, and Co-Pt electrodes with either Al_2O_3 or AlN barriers (as indicated in the plot) and superconducting counterelectrodes of $Al_{100-x}Si_x$ ($x \sim 2$–5). All measurements were taken at 0.25 K in a field of 2 T applied in the plane of the films. The values for the tunneling spin polarization (TSP) were extracted by fitting the data curves with the following additional fitting parameters indicated in the figure: superconducting gap △, depairing parameter ζ, and spin-orbit parameter b.

netic moment of a ferromagnetic material have distinct physical origins, the existence of such a relationship between these two properties has always been surprising. While the magnitude of the magnetic moment of a ferromagnetic material is related to the difference in the number of occupied spin up and spin down states below the Fermi level, the TSP of transition metals is generally believed to be due to electrons tunneling from the *sp* states near the Fermi level [16,17].

Our TSP measurements on Co-Pt alloys with Al_2O_3 barriers suggest that a linear correlation between TSP and *m* for transition metal alloys is not always true [see inset of Fig. 1(a)]. Indeed, we find that while the TSP for Co-Pt remains constant within experimental error up to a Pt fraction of at least 40%, the magnetization is strongly reduced. Typical STS data are shown in Figs. 2(a)–2(c) for Co, $Co_{60}Pt_{40}$, and $Co_{75}V_{25}$ electrodes together with fits to the data from which the polarization was extracted. For higher Pt content ($> 40\%$) the TSP decreases but even for $Co_{26}Pt_{74}$ is still substantial (~19%). No spin polarization was found for pure Pt electrodes (in fields of up to 2 T). The variation of TSP with Pt content clearly differs from the approximate linear decrease of the alloy atomic magnetic moment with increasing Pt fraction.

Since the TMR of MTJs is related to the TSP of the corresponding ferromagnetic electrodes [7], the large and similar values of TSP measured at 0.25 K for Co-Pt alloys for *x* ranging from 0 up to ~40% should be reflected in large and similar low temperature TMR values for MTJs containing these alloys. This is confirmed experimentally as shown in Fig. 3(a) which compares TMR data for two MTJs composed of an exchange biased $Co_{84}Fe_{16}$ electrode below an Al_2O_3 tunnel barrier with Co and $Co_{60}Pt_{40}$ counterelectrodes, respectively. While at low temperature the TMR values are very similar, the TMR decreases with increasing temperature in both cases, which is most likely due to a reduction of the magnetic moment at the electrode interfaces by thermally excited spin waves [18]. Since the reduction of the surface magnetic moment is larger for ferromagnetic electrodes with lower Curie temperatures, it is not surprising that the TMR of the MTJ with the

$Co_{60}Pt_{40}$ electrode decreases more rapidly with temperature than that with the Co electrode.

The near invariance of the TSP for Co-Pt alloys with up to ~40 at. % Pt might be explained by the segregation of Co to the Al_2O_3 interface since it is well known that the TSP strongly depends on the tunnel barrier interface [19,20]. However, detailed angle resolved x-ray photoemission spectroscopy (XPS) studies, which were carried out at the Co $2p_{3/2}$ and Pt $4d$ edges of a $Co_{60}Pt_{40}$ alloy film covered with a ~25 Å thick Al_2O_3 layer, rule out this possibility. By varying the emission angle of the photoelectrons, the Co-Pt composition was probed as a function of depth beneath the Al_2O_3 layer and no evidence for Co segregation was found.

The simplest explanation for the high TSP for Pt rich Co-Pt alloys measured using Al_2O_3 tunnel barriers is that the tunneling rate from Pt atomic sites is much lower than that from Co atomic sites so that tunneling from highly spin polarized Co sites dominates the tunneling current. The possibility of different tunneling rates from neighboring atomic sites is supported by spin polarized scanning tunneling microscopy (STM) studies in which it has been demonstrated that individual atoms can be imaged at alloy surfaces even when there is no topological contrast [21–23]. In particular, individual Ni and Pt atoms at a $Ni_{25}Pt_{75}(111)$ surface, which have similar d densities of states at the Fermi level, and little geometrical contrast, can yet be chemically resolved in an STM [22]. Thus these STM studies clearly support the notion that tunneling can vary strongly on the atomic scale even from highly metallic surfaces where the electron wave functions are delocalized.

Calculations show that the bonding of Co with oxygen can strongly influence spin-dependent tunneling from Co and that the formation of Co-O bonds can even result in a change in sign of the TSP from the minority to the observed majority spin character [24]. Since the chemical bond strength of oxygen with Co is much stronger than with Pt [25,26] it seems very reasonable to assume that the tunneling rate from Co sites is likely to be significantly higher than from Pt sites at the Co-Pt/Al_2O_3 interface [22]. The notion that Co and not Pt forms an oxygen bond is supported by our XPS studies which show that Co but not Pt at the tunnel barrier interface is partially oxidized.

If, indeed, the tunneling rate from Pt were significantly lower than that from Co, then the tunneling resistance for otherwise identical tunnel junctions should increase with an increasing Pt fraction of the Co-Pt electrode. Figure 3(b) shows the resistance measured for MTJs with one $Co_{84}Fe_{16}$ and one $Co_{1-x}Pt_x$ electrode as a function of Pt content. Each data point is the result of averaging over ~100 tunnel junctions with large and similar TMR values. The experiment was performed by fabricating in one batch two sets of identical MTJs with either Co or with a particular Co-Pt alloy electrode (~ 50 junctions/set). Since the resistance of nominally identical MTJs can vary from run to run due to small variations in the Al_2O_3 thickness, the resistance is normalized to the average resistance of the companion set of MTJs with Co electrodes. The data in Fig. 3(b) clearly show that the resistance of the MTJs increases by about 30% as the Pt content of the Co-Pt electrode is increased by 40%, consistent with the notion that tunneling from Pt is smaller as compared to tunneling from Co.

Having established that the tunneling rates from Co and Pt sites are very different, we can develop a simple model to account for the detailed dependence of TSP on the Pt concentration as shown in Fig. 1(b). We assume that the tunneling current is the sum of contributions from the Co and Pt sites where the current from each site is assumed to be proportional to the tunneling probability for electrons from this specific site. We also assume that the spin polarization of the tunneling current from the Co sites varies little as the Pt content of the alloy is increased. This is a reasonable assumption given that both magnetization and XMCD data show that the Co magnetic moment in Co-Pt alloys is not very different from pure Co. The overall spin polarization is then simply the spin polarization of Co weighted by the contribution of the Co sites to the overall tunneling current. The fit is shown as a dotted line in Fig. 1(b) and gives a tunneling probability from the Pt sites ~3.8 times lower than from the Co sites. This result is consistent with our supposition that electrons tunnel predominantly from highly spin polarized Co sites at the Al_2O_3 interface. Using the same model and the value of 3.8 for the ratio of tunneling probability from Co to Pt obtained from fitting the polarization data, the resistance change for MTJs with various Co-Pt electrodes can be calculated. This calculation is shown as a dashed line in Fig. 3(b) and accounts reasonably well for the observed trends in the data, given the simplicity of the model. It is interesting to note that the enthalpy of formation of CoO

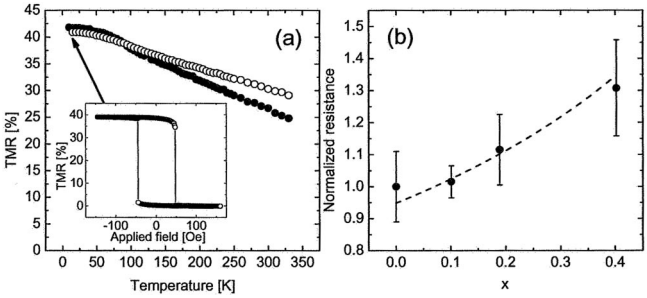

FIG. 3. (a) The temperature dependence of TMR for MTJs with an exchange biased $Co_{84}Fe_{16}$ electrode and a Co (○) or a $Co_{60}Pt_{40}$ (●) counterelectrode and Al_2O_3 tunnel barriers. A typical TMR loop is shown in the inset. (b) Dependence of normalized resistance of nominally identical magnetic tunnel junctions with a fixed $Co_{84}Fe_{16}$ electrode and a counterelectrode formed from various $Co_{1-x}Pt_x$ alloys on Pt fraction x. The dashed line shows the calculated resistance using a tunneling probability for tunneling from Pt sites that is lower by a factor of 3.8 as compared to the Co sites.

($\Delta H_f = -237$ kJ/mol) [25,27] is about 3.3 times higher than that for PtO ($\Delta H_f = -71$ kJ/mol) [27,28], indicating that the CoO bond strength is larger by a similar factor. Note that by contrast $\Delta H_f = -430$ kJ/mol for VO which is even higher than that for CoO [25].

An excellent test of the validity of these conclusions would be to compare results for a nonoxide tunnel barrier. To this end we have prepared STS structures with AlN barriers [see typical data in Fig. 2(d)]. TSP results for Co-V and Co-Pt electrodes are included in Fig. 1 (+ signs) and are compared with similar TSP data for Al_2O_3 barriers. For Co-Pt the data are quite different: the TSP decreases approximately linearly with Pt content for AlN barriers and fitting these data to the model described above yields very similar tunneling probabilities for Co and Pt, consistent with the expected lower reactivity of nitrogen for both Go and Pt as compared to oxygen [29]. These results suggest that it is, indeed, the bonding to oxygen in Al_2O_3 barriers that is responsible for the high TSP of Pt rich Co-Pt. Similarly, the less rapid decrease of TSP with V in Co-V alloys for AlN as compared to Al_2O_3 barriers is consistent with these arguments, as is the more rapid decrease of the TSP as compared to the magnetization in the latter case. (Note that the significantly larger TSP value for $Co_{95}V_5$ as compared to pure Co is likely due to a change in structure from fcc for pure Co to bcc upon small additions of V.)

In summary, we have demonstrated that the high spin polarization observed for Co-Pt alloys containing up to ~40 at. % Pt with Al_2O_3 barriers is related to much lower electron tunneling rates from Pt atomic sites as compared to Co atomic sites. This accounts for the lack of a correlation between spin polarization and magnetization for these alloys. Moreover, we find similar results for other alloys with Pt as well as with Pd: for example, the TSP of $Fe_{61}Pt_{39}$ is ~47% and that of $Fe_{66}Pd_{34}$ is ~41%. By contrast Co and Fe alloys containing, for example, V and Ru, show rapid decreases in spin polarization, even faster than the decrease of magnetization for these alloys. We propose that these very different behaviors can be attributed to the ease of formation of chemical bonds between the alloy constituents and oxygen in the tunnel barrier. These conclusions are supported by results for AlN barriers in which the TSP is found to linearly decrease with the addition of either V or Pt. These studies suggest that it is possible to form magnetic tunnel junctions with high spin polarization and correspondingly high tunneling magnetoresistance with low moment ferromagnetic alloy electrodes by manipulating the tunneling rates of the alloy constituents.

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*Present address: SFI Nanoscience Laboratory, Trinity College, Dublin 2, Ireland.
†Electronic address: parkin@almaden.ibm.com

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